

Universal representation of radial distribution for liquid metal phase

Koretaka Yuge¹

¹ *Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan*

A new representation of radial distribution for liquid metal phase under NVT ensemble is theoretically derived based on lattice statistical information (LSI) theory. We reveal that radial distribution for a given interatomic distance r can be essentially determined from two special microscopic states in liquid phase, which are independent both of temperature and atomic species. The present representation provides significant advantage in efficient and systematic investigation of atomic structures for liquid metal phases over existing approaches, that sweep across possible microscopic states over whole phase space.

Let us begin by considering the liquid phase, where its microscopic states are completely specified by a set of canonical variable q_i and p_i for M constituent particles (i represent particle index and M is constant). Then the corresponding partition function is given by

$$Z = \frac{1}{h^{3M}} \int \exp\left(-\frac{K+U}{k_B T}\right) d\Gamma, \quad (1)$$

where K and U denotes kinetic and potential energy. We assume Hamiltonian (H) for certain particle i is given by

$$H = \sum_j \frac{p_j^2}{2m} + U(\mathbf{q}). \quad (2)$$

This definition of H gives well-known equipartition law of energy through

$$\begin{aligned} \left\langle p_j \frac{\partial H}{\partial p_j} \right\rangle_Z &= Z^{-1} \int p_j \frac{\partial H}{\partial p_j} \exp(-\beta H) d\Gamma \\ &= Z^{-1} \int -\beta^{-1} p_j \frac{\partial}{\partial p_j} \exp(-\beta H) d\Gamma \simeq \beta^{-1}, \end{aligned} \quad (3)$$

where $\langle \rangle_Z$ denotes ensemble average and $\beta = (k_B T)^{-1}$ under the assumption that H approaches infinity with $|p_j| \rightarrow \infty$. When we consider the equilibrated large system with constant temperature T , ensemble average of kinetic energy of the system is therefore given by

$$\langle K \rangle_Z = \frac{3}{2} M k_B T. \quad (4)$$

Suppose for the large system, fluctuation of average kinetic energy over possible microscopic states would be neglected, then we rewrite

$$Z \simeq G \exp\left(-\frac{3}{2} M\right) \int \exp\left\{-\frac{U(\mathbf{q})}{k_B T}\right\} d\mathbf{q}, \quad (5)$$

where G is merely a normalized constant in accordance with the integral in momentum space. Therefore, expectation value of observable C independent of the momentum of microscopic states is generally given by

$$\langle C \rangle_Z \simeq \frac{\int C(\mathbf{q}) \exp\left\{-\frac{U(\mathbf{q})}{k_B T}\right\} d\mathbf{q}}{\int \exp\left\{-\frac{U(\mathbf{q})}{k_B T}\right\} d\mathbf{q}}. \quad (6)$$

Eq. (6) implies that LSI theory to obtain expectation value can be applied to liquid phase under appropriate variable transformation between \mathbf{q} and structural parameters. Our derivation below is based on Eq. (6).

Next, to describe atomic structure in liquid phase, we employ the well-known radial distribution function. Consider the system in liquid phase is in constant volume V and in constant number density ρ . Let us focus on a single particle i for a certain microscopic state, and define the number of particles, whose distance from particle i is between r and $r + dr$, as $n_i(r)$. Then the radial distribution function is given by

$$g(r) = \frac{\overline{n(r)}}{4\pi r^2 dr \rho}, \quad (7)$$

where $\overline{n(r)}$ denotes average of $n_i(r)$ over all constituent particles. Therefore the radial distribution function is a measure of average density in given distance r in terms of that in ideally random mixture. Practically, expectation value of the radial distribution function, $\langle g(r) \rangle_Z$, is required to determine atomic structure of the liquid phase. The goal of the present study is thus to derive a new representation of $\langle g(r) \rangle_Z$ based on lattice statistical information (LSI) theory,^{1,2} which would provide new insight into how radial distribution in liquid phase is ruled by distance r and would enable efficient estimation of $\langle g(r) \rangle_Z$ independent of the choice of constituent elements.

Let us divide the three dimensional system into equivalent and sufficiently small cubes, where each cube has a length of R on one side. When we interpret vertex of the cubes as lattice points, the number of lattice points in the system and number of particles are respectively given by V/R^3 and ρV . We define the composition x as

$$x = \frac{\rho V}{V/R^3}, \quad (8)$$

which represents fraction of the number of particles with respect to the number of lattice points. We then introduce spin variable σ_k , where $\sigma_k = +1$ denote occupation of lattice point k by particle and $\sigma_k = -1$ is a vacant site. With this definition, number of pair sites in distance between r and $r + dr$ is given by

$$N_{\text{pair}}(r) = S(r) \frac{V}{R^3}, \quad (9)$$

where

$$S(r) = \frac{2\pi r^2 dr}{R^3} \quad (10)$$

is the number of pair sites for one lattice point. When we focus on a certain particle i , number of vacant site in distance between r and $r + dr$ is

$$N_i(r) = \frac{4\pi r^2 dr}{R^3} - n_i(r). \quad (11)$$

Using above equations and definitions, structural parameter for pair figure in distance r used in the LSI theory can be given by

$$\xi(r) = \frac{-\rho V \overline{N(r)} + \left\{ S(r) \frac{V}{R^3} - \rho V \overline{N(r)} \right\}}{S(r) \frac{V}{R^3}}, \quad (12)$$

where $\overline{N(r)}$ denotes average of $N_i(r)$ over all particles. Using Eqs. (7)-(12), we can express radial distribution function by $\xi(r)$:

$$g(r) = \frac{1}{4x^2} \xi(r) + \left(\frac{1}{x} - \frac{1}{4x^2} \right). \quad (13)$$

From Eq. (13), it appears that $g(r)$ depends on artificially introduced length R , but below we see that final representation for *expectation value* of $g(r)$ is independent of R . It has been shown³ that pair structural parameter have the characteristic of

$$\langle \xi(r) \rangle = (2x - 1)^2, \quad (14)$$

where $\langle \rangle$ denotes average over all possible microscopic states. Using the fact from LSI theory¹ that density of microscopic states in terms of $\xi(r)$ is given by normal distribution function, we can confirm for average that

$$\langle \xi(r) \rangle = 4x^2 \langle g(r) \rangle - 4x + 1 = (2x - 1)^2, \quad (15)$$

since by definition of radial distribution, $\langle g(r) \rangle = 1$, and for

standard deviation,

$$\begin{aligned} \langle g(r) \rangle_{\text{sd}} &= \frac{1}{4x^2} \langle \xi(r) \rangle_{\text{sd}} \\ &= \frac{1}{4x^2} \frac{1}{\sqrt{\frac{V}{R^3} S(r)}} (-4x^2 + 4x) \\ &\simeq \frac{1}{\rho \sqrt{2\pi r^2 dr V}}, \end{aligned} \quad (16)$$

where $\langle \rangle_{\text{sd}}$ denotes standard deviation of density of microscopic states. To derive the last equation of Eq. (16), we consider the limit of $R \rightarrow 0$. Consider that radial distribution function $g(r)$ is merely a linear transformation of $\xi(r)$, expectation value of $g(r)$ should have the same form as that of $\xi(r)$ given in the LSI theory,² namely,

$$\langle g(r) \rangle_Z = \langle g(r) \rangle - \frac{\sqrt{2\pi}}{k_B T} \langle g(r) \rangle_{\text{sd}} \left\{ \langle E \rangle_r^{(+)} - \langle E \rangle \right\}, \quad (17)$$

Here, $\langle E \rangle$ is the potential energy of the special microscopic state that satisfies $g(r) = 1$ for any given r . $\langle E \rangle_r^{(+)}$ is the potential energy of another special microscopic state that has $\langle g(r') \rangle_r^{(+)}$ for any given r' , where $\langle \rangle_r^{(+)}$ denote average over all microscopic states under the condition of $g(r) \geq 1$. Substituting Eq. (16) into Eq. (17), we obtain the final form of radial distribution function:

$$\langle g(r) \rangle_Z = 1 - \frac{\langle E \rangle_r^{(+)} - \langle E \rangle}{k_B T \rho \sqrt{r^2 dr V}}. \quad (18)$$

We should emphasize here that atomic structures with energy of $\langle E \rangle_r^{(+)}$ and $\langle E \rangle$ are independent of both temperature and atomic species, since partial average $\langle g(r') \rangle_r^{(+)}$ and average $\langle g(r) \rangle$ for microscopic states are clearly independent of temperature and atomic species.

¹ K. Yuge, arXiv:1311.1664 [cond-mat.mtrl-sci] (2014).

² K. Yuge, arXiv:1408.7082 [cond-mat.mtrl-sci] (2014).

³ A. Zunger, S.-H. Wei, L.G. Ferreira, and J.E. Bernald, Phys. Rev.